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ORGANIC SEMICONDUCTOR

Abstract:

A solution processible intrinsically electrically conductive polymeric material, in particular, poly[octyl 1,2-(2',2''-dithienylacrylate)]. A method for forming the polymer is also defined.

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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number: PCT/AU96/00008</b> <b>(22) International Filing Date: 10 January 1996 (10.01.96)</b> <b>(30) Priority Data:</b> PN 0469 10 January 1995 (10.01.95) AU <b>(71) Applicants (for all designated States except US):</b> UNIVERSITY OF TECHNOLOGY, SYDNEY [AU/AU]; Broadway, NSW 2077 (AU). METAL MANUFACTURES LTD. [AU/AU]; 1 Heathcote Road, Liverpool, NSW 2170 (AU). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> CONN, Costa [AU/AU]; 24 Percival Road, Stanmore, NSW 2048 (AU). JIN, Zheshi [KR/AU]; 4/7 Janet Street, Jesmond, NSW 2299 (AU). UNSWORTH, Joseph [AU/AU]; 12 Wyuna Place, Dundas, NSW 2117 (AU). <b>(74) Agent:</b> F.B. RICE & CO.; 28A Montague Street, Balmain, NSW 2041 (AU).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title: ORGANIC SEMICONDUCTOR</b>  <b>(57) Abstract</b>  A solution processible intrinsically electrically conductive polymeric material, in particular, poly{octyl 1,2-(2',2''-dithienylacrylate)}. A method for forming the polymer is also defined.		

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## ORGANIC SEMICONDUCTOR

### Field of the Invention

The present invention relates generally to organic semiconductors and methods for their preparation and in particular to an intrinsically  
5 electrically semiconducting polymeric material. Intrinsically semiconducting polymer material has potential application in a wide range of electronic and opto-electronic devices.

### Background Art

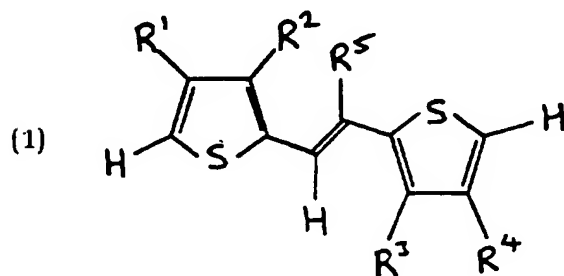
A number of intrinsically conducting polymers have been well  
10 known for over a decade. One of the most extensively characterised conducting polymers is polyacetylene. This polymer possesses a backbone with a high degree of unsaturation leading to  $\pi$ -orbital overlap and electron delocalisation. This delocalisation allows the polymer to possess a quite remarkable electrical conductivity when compared with traditional  
15 insulating polymers. The structure of polyacetylene does, however, render the polymer quite unstable.

Another common class of intrinsically conducting polymers are the polyheterocyclics, such as polypyrrole and polythiophene. In the case of polypyrrole, the repeat unit of this polymer is comprised of a 5-membered  
20 cyclic ring with two delocalised  $\pi$  bonds and a nitrogen heteroatom. Polypyrrole when produced using an electrochemical process can form a free standing film with electrical conductivity as high as 100 S/cm. Polyheterocyclics possess an improved environmental stability in comparison to that of polyacetylene, the improved stability being provided  
25 by the aromatic nature of the heterocyclic ring which prevents loss of  $\pi$  bond unsaturation.

Despite there being a quite large number of postulated applications for intrinsically conducting polymers, this has to date been limited by a number of undesirable properties such as poor processibility and poor  
30 solubility thereby preventing processing of the polymers using traditional processing techniques. The conducting polymers described above are also typically opaque thereby limiting their opto-electronic applications.

Disclosure of the Invention

According to a first aspect, the present invention consists in a chemical compound having the formula:

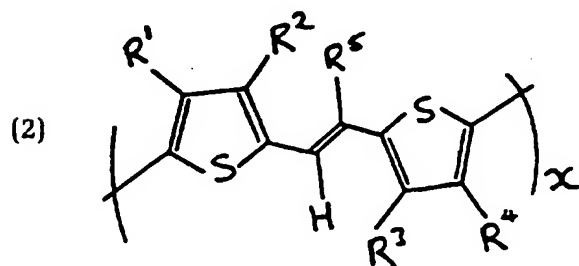


wherein  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are electron donating substituents or hydrogen and  $R^5$  is an electron withdrawing substituent.

The electron donating substituents are preferably straight-chain, branched-chain or cyclic alkyl or alkoxy groups which may be unsubstituted or substituted to an extent that does not remove their electron donating properties. The alkoxy groups are preferably any  $C_1$ - $C_{18}$  alkoxy chain in any combination and most preferably a  $-(CH_2)_nCH_3$  or  $-O(CH_2)_nCH_3$  group where  $n = 0-17$ .

The electron withdrawing substituent  $R^5$  is preferably a carboxylic acid group, an ester group, a cyano group, a nitro group, an aldehyde, a sulphonic acid or a halogen. The carboxylic acid group is preferably a  $-CO_2H$  or  $-CO_2(CH_2)_nCH_3$  group, where  $n = 0-17$ .

According to a second aspect, the present invention consists in a polymer having the formula:



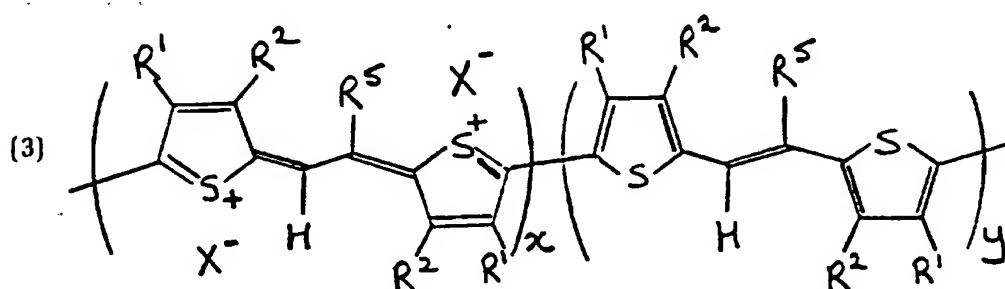
wherein  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are electron donating substituents or hydrogen,  $R^5$  is an electron withdrawing substituent and  $x$  is the number of monomeric units comprising the polymer.

The electron donating substituents are preferably straight-chain, branched-chain or cyclic alkyl or alkoxy groups which may be unsubstituted or substituted to an extent that does not remove their electron donating properties. The alkoxy groups are preferable any  $C_1$ - $C_{18}$  alkoxy chain in any combination and most preferably a  $-(CH_2)_nCH_3$  or  $-O(CH_2)_nCH_3$  group where  $n = 0-17$ .

The electron withdrawing substituent  $R^5$  is preferably a carboxylic acid group, an ester group, a cyano group, a nitro group, an aldehyde, a sulphonic acid or a halogen. The carboxylic acid group is preferably a  $-CO_2H$  or  $-CO_2(CH_2)_nCH_3$  group where  $n = 0-17$ .

The number of monomeric units  $x$  preferably lies in the range 5-200 and the polymer is preferably poly[octyl 1,2-(2',2''-dithienylacrylate)] (PODA).

According to a third aspect, the present invention consists in a doped form of polymer (2) having the formula:



wherein  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are electron donating substituents or hydrogen,  $R^5$  is an electron withdrawing substituent,  $X$  is a dopant anion and  $x + y$  is the total number of monomeric units.

The electron donating substituents are preferably straight-chain, branched-chain or cyclic alkyl or alkoxy groups which may be unsubstituted or substituted to an extent that does not remove their electron donating

properties. The alkoxy groups are preferably any C<sub>1</sub>-C<sub>18</sub> alkoxy chain in any combination and most preferably a  $-(CH_2)_nCH_3$  or  $-O(CH_2)_nCH_3$  group where  $n = 0-17$ .

5 The electron withdrawing substituent R<sup>5</sup> is preferably a carboxylic acid group, an ester group, a cyano group, a nitro group, an aldehyde, a sulphonic acid or a halogen. The carboxylic acid group is preferably a  $-CO_2H$  or  $-CO_2(CH_2)_nCH_3$  group where  $n = 0-17$ .

The number of monomeric units  $x + y$  preferably lies in the range 5-200.

10 According to a further aspect, the present invention comprises a method for forming polymer having the formula (2) comprising polymerising monomer units having the formula (1).

The polymer is preferably formed using either a chemical or electrochemical method.

15 The chemical method preferably comprises chemical polymerisation of the monomeric units by a suitable oxidant. The oxidants are preferably  $SbCl_5$ ,  $FeCl_3$ ,  $Fe(ClO_4)_3$  or  $Fe(4-CH_3C_6H_4SO_3)_3$ . During polymerisation, the polymer is preferably "doped" by an anion derived from the oxidant. The oxidant concentration preferably lies in the range 0.1M to 1M.

20 The electrochemical method preferably comprises a galvanostatic, potentiostatic or potentiodynamic oxidative method wherein the monomers are polymerized in an organic solvent with the resulting polymer deposited on an anode of an electrochemical cell. The organic solvent preferably includes propylene carbonate, dichloromethane, acetonitrile or benzonitrile. During electrochemical polymerization, the polymer electrostatically incorporates dopant anions which provide polymer charge neutrality. The dopant anions preferably include one of the following:

25  $BF_4^-$ ,  $ClO_4^-$ , aryl- $SO_3^-$ ,  $PF_6^-$ ,  $HSO_4^-$ ,  
 $NO_3^-$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $AsF_6^-$ ,  $I_3^-$ ,  $FeCl_4^-$   
 30 or  $Fe[(CN)_6]^{3-}$ .

Following polymerization, the polymer is preferably reduced to facilitate its dissolution in an organic solution. Following chemical polymerization, the polymer is dedoped and reduced by exposing the polymer to a suitable agent, preferably ammonia or hydrazine. Following electrochemical polymerization, the polymer is preferably left in situ on the electrode and the polarity of the electrochemical cell is reversed.

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The reduced polymer formed using either the electrochemical or chemical method is preferably soluble in tetrahydrofuran or chloroform. The polymer solution is preferably processed to form thin films of polymer. The processing preferably comprises a spin-coating method in which the polymer is cast onto a substrate to form a thin film. The substrate preferably forms an electrical contact with the polymer and preferably includes metals, indium-tin oxide coated glass or direct band-gap semiconductors, for example, indium phosphide, gallium arsenide, and indium gallium arsenide. The electrical contact can be made either ohmic or rectifying as required.

The polymer thin films are preferably translucent or transparent and can be re-oxidised in a suitable oxidant solution. When reduced the polymer preferably has an electrical conductivity of approximately  $10^{-8}$  S/cm and when oxidised an electrical conductivity of approximately  $10^{-3}$  S/cm. The polymer thin films can be utilised in electronic and opto-electronic devices, including photodiodes (e.g. p-i-n diodes), light emitting diodes (LEDs), wave guides, optical switches, gas-sensors, solar cells and Schottky junctions.

#### Best Method of Performing the Invention

By way of example only, preferred embodiments of the invention are described below.

#### Example 1 - Method for the Production of a Chemical Compound having Formula (1)

A method for the production of a chemical compound (1) where  $R^1=R^2=R^3=R^4=H$  and  $R^5=CO_2(CH_2)_7CH_3$  is as follows:

At a temperature of  $-78^\circ C$  under an argon atmosphere, a solution of 5g octyl(thiophene-2-acetate) in 5ml tetrahydrofuran is slowly added to a solution of 2.10g lithium diisopropylamide in 100ml tetrahydrofuran. After stirring at  $-78^\circ C$  for 30 minutes, 1.92g of thiophene-2-carboxaldehyde is added and the resulting solution is stirred for a further 30 minutes at  $-78^\circ C$ . The resultant solution is slowly allowed to warm to  $20^\circ C$  and is then poured into 100ml of 5% hydrochloric acid. This mixture is then extracted 3 times with 50ml diethyl ether and the combined ether extracts are dried over sodium sulphate and concentrated in vacuo. To this residue is added 500ml of dry benzene and 0.1g of para-toluene sulphonic acid. This solution is then heated to reflux for 6 hours. On cooling, the solution is washed twice with 100ml of water and then dried over sodium sulphate. The benzene is then removed by evaporation and the resultant yellow residue is



chromatographed to afford a compound having the formula (1) where  $R^1=R^2=R^3=R^4=H$  and  $R^5=CO_2(CH_2)_7CH_3$ . This material can be recrystallised from methanol to form pale yellow needles.

#### Example 2 - Polymerisation

5           Compound (1) having  $R^1=R^2=R^3=R^4=H$  and  $R^5=CO_2(CH_2)_7CH_3$  can be polymerised using the following procedure:

To a stirred solution of 2.0g of compound (1) having  $R^1$  to  $R^5$  as defined above in 100ml of dry chloroform is added 1.86g of anhydrous iron (III) chloride, with the resulting solution being stirred at 20°C for 20 hours.  
10   Following this, 50ml of 5% aqueous ammonia solution is added and after 30 minutes the two layers are separated with the chloroform layer washed twice with 50ml of water. After drying over sodium sulphate and being concentrated in vacuo, the resultant red-brown residue is washed with methanol in a Soxhlet apparatus. This procedure affords a polymer having  
15   the formula (2) where  $R^1=R^2=R^3=R^4=H$  and  $R^5=CO_2(CH_2)_7CH_3$ .

#### Example 3 - Thin Film Preparation

Solutions of different concentrations of the polymer having formula (2) where  $R^1=R^2=R^3=R^4=H$  and  $R^5=CO_2(CH_2)_7CH_3$ , namely 5mg/ml, 10mg/ml, 15mg/ml, 20mg/ml and 30mg/ml, in tetrahydrofuran were prepared  
20   to obtain thin films with a range of thicknesses. Solutions with high concentrations were prepared by blowing off solvent with high purity nitrogen gas thereby affording thick films. Prior to coating the solutions were passed through filters with a porosity of 0.25 microns.

Thin films of the polymer having formula (2) were prepared using a  
25   Photo Resist Spinner in a clean air workstation. Sapphire slides were employed as substrates because of the excellent thermal conductivity of sapphire which is important for measurements at various temperatures. The slides were cleaned by soaking in chromic acid at 80°C for 15 minutes followed by thorough rinsing with double distilled water and finally blown  
30   dry with high purity nitrogen. To optimise the spinning conditions, the solutions were first spin coated at different speeds ranging from 500 rpm to 4000 rpm. It was found that the film thickness decreases with spin speed for all concentrations indicating that a lower spin speed gives a thicker film. It was found, however, that when the spin speed was too low (ie less than 1000  
35   rpm) the films were not continuous. The spin speed was, therefore, set at 1000 rpm. By spinning at 1000 rpm for 40 seconds, films of thickness

ranging from 20 nm to 1000 nm were obtained. The thickness was measured using multiple beam interferometry. The films are transparent and deep orange in colour.

#### Example 4 - Doping of the Films

5           A 0.2 molar solution of anhydrous ferric chloride in anhydrous acetonitrile was used as the doping medium. The dopant solution was kept in a well sealed container and stored in a desiccator. The doping process was carried out by immersing the thin films in the dopant solution for a desired period followed by a thorough rinsing with anhydrous acetonitrile.  
10       When undoped, the film showed an electrical conductivity of  $10^{-8}$  S/cm and the conductivity increased logarithmically with doping up to  $10^{-3}$  S/cm.

#### Example 5 - Fabrication of Ohmic Contact

          Ohmic contacts in a sandwich configuration were produced with platinum as the electrode material. The contact area was  $0.2 \text{ cm}^2$ . For the  
15       bottom electrode, platinum with a thickness of about 100 nm was DC vacuum sputtered using a Sputter Coating Unit onto the freshly cleaned sapphire substrate and polymer films having the formula (2) with thicknesses of 400 nm were immediately spin coated on top of the electrode.

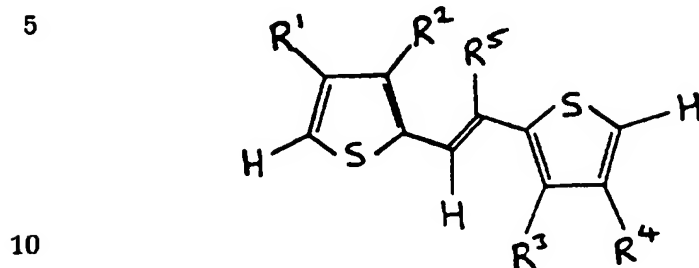
          The thin film was then heated in vacuum at  $60^\circ\text{C}$  for ninety minutes  
20       to remove any organic residue. For the top electrode, platinum was DC Vacuum Sputtered by multiple sputtering of a semi-transparent film of platinum with a very short single sputtering time of 0.3 seconds to avoid heating and consequent damage of the polymer films. The contacts were stable at various temperatures and reproducible.

25       The polymer films have potential application in a wide range of electronic and opto-electronic devices including light emitting diodes, wave guide, optical switches, gas sensors, solar cells and Schottky junctions.

          It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in  
30       the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

## CLAIMS:

1. A chemical compound having the formula:



15 wherein  $R^1, R^2, R^3$  and  $R^4$  are electron donating substituents or hydrogen and  $R^5$  is an electron withdrawing substituent.

2. The chemical compound of claim 1 wherein the electron donating substituents are straight-chain, branched-chain or cyclic alkyl or alkoxy groups.

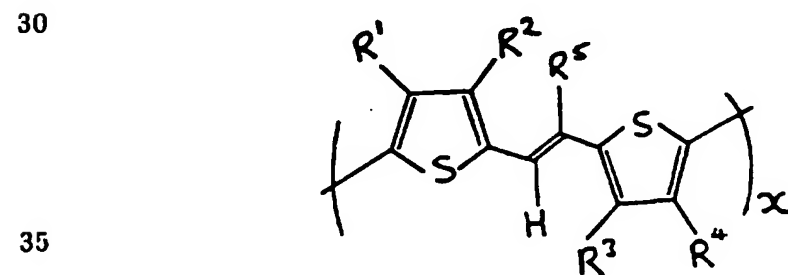
3. The chemical compound of claim 2 wherein the alkoxy groups are any  $C_1$ - $C_{18}$  alkoxy chain.

4. The chemical compound of claim 3 wherein the alkoxy chain is a  $-(CH_2)_nCH_3$  or a  $-O(CH_2)_nCH_3$  group where  $n = 0-17$ .

5. The chemical compound of claim 1 wherein the electron withdrawing substituent  $R^5$  is a carboxylic acid group, an ester group, a cyano group, a nitro group, an aldehyde, a sulphonic acid or a halogen.

6. The chemical compound of claim 5 wherein the carboxylic acid group is a  $-CO_2H$  or a  $-CO_2(CH_2)_nCH_3$  group. where  $n = 0-17$ .

7. A polymer having the formula:



wherein  $R^1, R^2, R^3$  and  $R^4$  are electron donating substituents or hydrogen,  $R^5$  is an electron withdrawing substituent and  $x$  is the number of monomeric units comprising the polymer.

8. The polymer of claim 7 wherein the electron donating substituents are straight-chain, branched-chain or cyclic alkyl or alkoxy groups.

9. The polymer of claim 8 wherein the alkoxy groups are any  $C_1$ - $C_{18}$  alkoxy chain.

10. The polymer of claim 9 wherein the alkoxy chain is a  $-(CH_2)_nCH_3$  or a  $-O(CH_2)_nCH_3$  group where  $n = 0-17$ .

11. The polymer of claim 7 wherein the electron withdrawing constituent  $R^5$  is a carboxylic acid group, an ester group, a cyano group, a nitro group, an aldehyde, a sulphonic acid or a halogen.

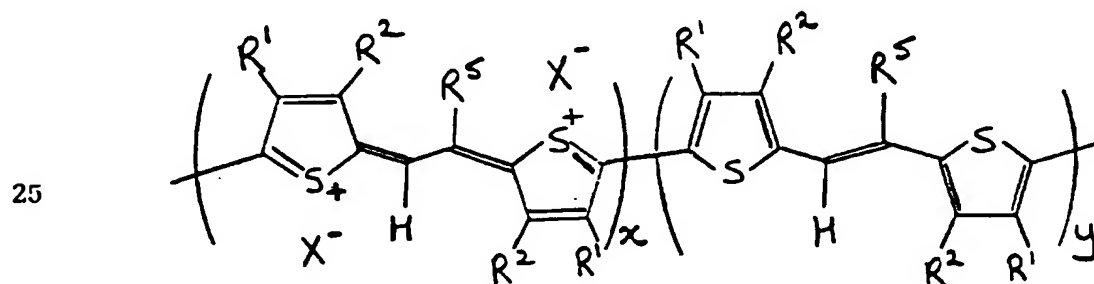
12. The polymer of claim 11 wherein the carboxylic acid group is a  $-CO_2H$  or a  $-CO_2(CH_2)_nCH_3$  group where  $n = 0-17$ .

13. The polymer of claim 7 wherein the number of monomeric units  $x$  lies in the range 5-200.

14. The polymer of claim 7 wherein the polymer is poly[octyl 1,2-(2',2"-dithienylacrylate)].

15. A doped polymer having the formula:

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30 wherein  $R^1, R^2, R^3$  and  $R^4$  are electron donating substituents or hydrogen,  $R^5$  is an electron withdrawing substituent,  $X$  is a dopant anion and  $x+y$  is the total number of monomeric units.

16. The doped polymer of claim 15 wherein the electron donating substituents are straight-chain, branched-chain or cyclic alkyl or alkoxy groups.

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17. The doped polymer of claim 16 wherein the alkoxy groups are any  $C_1$ - $C_{18}$  alkoxy chain.

18. The doped polymer of claim 17 wherein the alkoxy chain is a  $-(CH_2)_nCH_3$  or a  $-O(CH_2)_nCH_3$  group where  $n = 0-17$ .

5 19. The doped polymer of claim 15 wherein the electron withdrawing substituent  $R^5$  is a carboxylic acid group, an ester group, a cyano group, a nitro group, an aldehyde, a sulphonic acid or a halogen.

20. The doped polymer of claim 19 wherein the carboxylic acid group is a  $-CO_2H$  or a  $-CO_2(CH_2)_nCH_3$  group where  $n = 0-17$ .

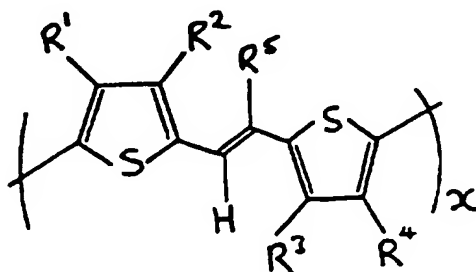
10 21. The doped polymer of claim 15 wherein the number of monomeric units  $x + y$  lies in the range 5-200.

22. The doped polymer of claim 15 wherein the electrical conductivity is in the range  $10^{-8}S/cm$  to  $10^{-3}S/cm$ .

23. A method for forming a polymer having the formula:

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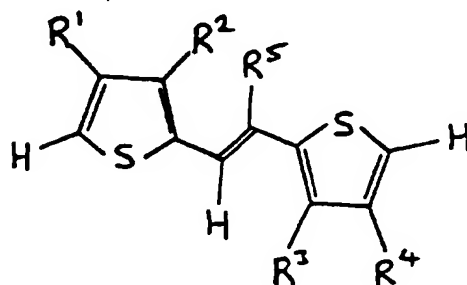


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comprising polymerising monomer units having the formula:

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24. The method of claim 23 wherein the polymer is formed using either a chemical or electrochemical method.
25. The method of claim 24 wherein the chemical method comprises chemical polymerisation of the monomeric units by exposure to an oxidant.
- 5 26. The method of claim 25 wherein the oxidants are selected from  $\text{SbCl}_5$ ,  $\text{FeCl}_3$ ,  $\text{Fe}(\text{ClO}_4)_3$  or  $\text{Fe}(4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3)_3$ .
27. The method of claim 24 wherein the electrochemical method comprises a galvanostatic, potentiostatic or potentiodynamic oxidative method wherein the monomers are polymerised in an organic solvent with
- 10 the resulting polymer deposited on an anode of an electrochemical cell.
28. The method of claim 27 wherein the organic solvent is either propylene carbonate, dichloromethane, acetonitrile or benzonitrile.
29. The method of claim 27 wherein during electrochemical polymerisation, the polymer electrostatically incorporates dopant anions
- 15 which provide polymer charge neutrality, the dopant anions including one of the following groups:
- $\text{BF}_4^-$ ,  $\text{ClO}_4^-$ , aryl- $\text{SO}_3^-$ ,  $\text{PF}_6^-$ ,  $\text{HSO}_4^-$ ,  
 $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{AsF}_6^-$ ,  $\text{I}_3^-$ ,  $\text{FeCl}_4^-$   
or  $\text{Fe}[(\text{CN})_6]^{3-}$ .
- 20 30. The method of claim 24 wherein following polymerisation, the polymer undergoes the following processing steps:
- (i) reduction;
- (ii) dissolution in tetrahydrofuran or chloroform; and
- (iii) casting onto a substrate using a spin-coating method to form a thin
- 25 film.
31. The method of claim 30 wherein the substrate forms an electrical contact with the polymer.

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/AU 96/00008

## A. CLASSIFICATION OF SUBJECT MATTER

Int Cl<sup>6</sup>: C07D 333/12, 333/22, 333/24, 333/32, C08G 75/06, H01L 51/30

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl<sup>6</sup>: C07D 333/12, 333/22, 333/24, 333/32

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
AU: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
CAS On-Line, substructure search  
DERWENT, IPC as above and keyword "polymer"

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4711742 (KWAN-YUE A. JEN et al.), 8 December 1987 (8.12.87)	1-31
A	US, A, 5268448 (W. BUECHNER et al), 7 December 1993 (7.12.93)	1-31
A	DE, A, 4223810 (BASF AG), 27 January 1994 (27.01.94)	1-31



Further documents are listed in the continuation of Box C



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International Application No.

**PCT/AU 96/00008**

<b>C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
<b>Category*</b>	<b>Citation of document, with indication, where appropriate, of the relevant passages</b>	<b>Relevant to claim No.</b>
A	Derwent Accession Number 94-307630, JP, A, 06-234760 (MITSUBISHI PAPER MILLS LTD), 23 August 1994 (23.08.94)	1-31



**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International Application No.  
**PCT/AU 96/00008**

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
US	4711742	EP	203438	JP	61-278526		
US	5268448	AT	116981	DE	69015906	EP	408105
		FR	2649396	JP	03-103428		
END OF ANNEX							

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